VI.8 Sorbents for Desulfurization of Natural Gas and LPG

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Objectives

- Develop a low-cost, high-capacity, expendable sorbent that can reduce the concentration of organic sulfur species in natural gas and liquefied petroleum gas (LPG) to less than ppb levels.
- Develop a regenerable version of the sorbent for large-scale stationary power generation applications.
- Scale up sorbent production using commercial manufacturing equipment.
- Demonstrate combined operation of the desulfurizer with a solid oxide fuel cell (SOFC).
- Carry out an independent engineering analysis to fully assess the potential of the new desulfurization sorbent.

Approach

- Carry out bench-scale screening tests to identify materials that adsorb organic sulfur species with high capacity.
- Perform parametric experiments with selected sorbents to optimize operating conditions.
- Demonstrate the regeneration potential and long-term durability of the best sorbent through many consecutive adsorption/regeneration cycles.
- Produce larger batches of the new material using high-throughput equipment (e.g., spray dryers, screw extruders) representative of commercial production.
- Establish partnerships with SOFC technology developers in the Solid State Energy Conversion Alliance (SECA) to demonstrate the potential of the new desulfurization sorbent in combination with SOFCs.
- Based on the performance results, assess the technical and economical impact of the new materials in SOFC-based distributed and stationary power generation systems.

Accomplishments

- *TDA's SulfaTrap™ sorbent achieves a sulfur capacity greater than 3.12% wt. (lb of sulfur removed per lb of sorbent).*
  In our accelerated bench-scale screening experiments, we identified a sorbent that can remove organic sulfur compounds from natural gas with high capacity. The sorbent reduces the sulfur content to less than 50 ppbv and tolerates the presence of water vapor and CO_2 impurities in the gas.
- *TDA's SulfaTrap™ sorbent maintained stable performance in a 10-cycle test.*
  We demonstrated that the sorbent can be regenerated by applying a mild temperature swing: heating up the bed to 350°C. Through 10 consecutive adsorption/regeneration cycles, the sorbent achieved a stable adsorption capacity and the pellets maintained their mechanical integrity.

- *Performance of TDA's SulfaTrap^{TM} sorbent was demonstrated in combination with a 5-kW$_e$ SOFC.* TDA supplied a 2.2 L batch of its sorbent to Siemens Westinghouse Power Corporation (SWPC). TDA's SulfaTrap^{TM} sorbent successfully removed all the sulfur from the pipeline natural gas during the 2,700-hr alpha test at SWPC's Research Center in Pittsburg, Pennsylvania.
- *A modified version of the sorbent successfully desulfurizes LPG.* TDA's sorbent achieves a 2.65% wt. sulfur capacity to desulfurize commercial LPG. It has been shown that less than 20 cc sorbent can desulfurize a 20-lb commercial LPG tank.

Future Directions

- *Develop a 125-kW$_e$ desulfurizer for SWPC.* This unit will be tested in the field at SWPC's customer site. The sorbent production will be scaled up to meet the requirement.
- *Demonstrate the long-term stability of the sorbent.* We will carry out a 100-cycle test to demonstrate sorbent life under representative conditions.
- *Assess the economic impact.* In collaboration with J. Thiessen, LLC, assess the techno-economic impact of the new technology.

Introduction

Advances in fuel cell technologies, together with the widespread restructuring of the power industry, have the potential to revolutionize the way power is produced and distributed. Distributed power generation is becoming a viable economic alternative to buying power from a central grid. In order to reach commercial potential in any of these markets, there must be an ample supply of high-quality fuel.

Pipeline natural gas is the fuel of choice for fuel-cell-based distributed power generation systems because of its abundant supply and well-developed infrastructure. However, effective utilization of natural gas in fuel cells requires that sulfur impurities (naturally occurring sulfur compounds and sulfur-bearing odorants) be removed to prevent them degrading the performance of the fuel cell stacks and poisoning the catalysts used in the fuel processor. Sulfur removal is important in all types of fuel cells. Even the more sulfur-tolerant SOFCs need the sulfur content of the natural gas to be reduced. TDA Research, Inc. (TDA) is developing a low-cost, high-capacity sorbent that can remove odorants from natural gas and LPG and enable effective utilization of natural gas in fuel cells.

Approach

While there are large-scale commercial technologies (e.g., hydrodesulfurization) that can remove organosulfur compounds to levels that fuel cells can tolerate, they are far too complex and expensive for small-scale systems. Most developers of the small-scale fuel cell systems prefer to remove sulfur from the feed gases using expendable (once-through) sorbents that operate at ambient temperature (a simple addition to the overall fuel cell system). For large-scale stationary systems, the use of regenerable sorbents that increase utilization is also considered a viable approach. In our work, we first prepared a large number of formulations and carried out bench-scale screening tests to identify materials that adsorb sulfur-bearing odorants with high capacity. We then performed parametric experiments with selected sorbents to optimize the conditions for their operation. We demonstrated the long-term durability and regeneration potential of the best sorbent formulation through many consecutive adsorption/regeneration cycles. In the future, we will produce larger batches of the new material using high-throughput equipment (e.g., spray dryers, screw extruders) representative of commercial production, and demonstrate the potential of the new desulfurization sorbents in combination with SOFCs. Based on the field performance results, we will assess the technical and economical impact of the new materials in distributed and stationary power generation systems.

Results

In extensive screening tests, we compared the performance of our sorbent with a number of commercial and specially prepared physical adsorbents, including several samples supplied by SWPC. In 2000, SWPC initiated a test program to identify a strategic supplier for a natural gas desulfurization process and carried out extensive engineering tests to evaluate potential desulfurization sorbents [1]. The most promising sorbents identified in SWPC's study were further tested to compare their performance to that of the new materials developed at TDA. Some of these sorbents were cerium and copper exchanged zeolite-Y, respectively, prepared to be similar to those reported by University of Michigan [2], Pennsylvania State University [3] and Pacific Northwest National Laboratory [4]. For quick comparison, accelerated tests were carried out at a high gas hourly space velocity (GHSV) of 60,000 h^{-1} (corresponding to very short gas-solid contact times). The performance of each sorbent was evaluated at an identical baseline condition; the sulfur-laden natural gas stream contained 12.3 ppmv dimethyl sulfide (DMS), 8.9 ppmv tert-butyl mercaptan (TBM), and 8.9 ppmv tetrahydrothiophene (THT). These higher-than-pipeline-gas sulfur concentrations and short contact times allowed observation of the breakthrough profiles of these odorants in relatively short times. TDA's SulfaTrap^{TM} sorbent showed the best performance, achieving a pre-breakthrough sulfur capacity of 3.12% wt. while reducing the sulfur concentration of the natural gas to less than 50 ppbv (the pre-breakthrough sulfur adsorption capacity is defined as the lb of total sulfur adsorbed per lb of sorbent when the breakthrough of the first sulfur compound was observed). Figure 1 shows the breakthrough profile of DMS for various sorbents, and Table 1 lists their sulfur capacities.

We evaluated the effect of water on the performance of various sorbents. Typical U.S. pipeline natural gas may contain up to 155 ppmv of water vapor (~7 lbs of water per million cubic feet of natural gas). It is anticipated that competition by water vapor for adsorption sites reduces the sulfur capacity of activated carbon and zeolite based sorbents in real-world applications due to their affinity to water. Therefore, some of the samples were evaluated using a gas stream containing 45 ppmv water vapor with all other gas concentrations remaining identical (i.e., 12.3 ppmv DMS, 8.9 ppmv TBM and 8.9 ppmv THT at a GHSV of 60,000 h^{-1}).

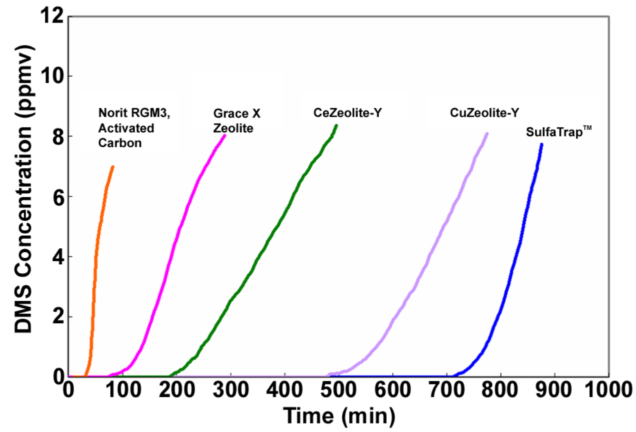

Figure 1. Comparison of Sulfur Removal Performance of TDA's SulfaTrap^{TM} Sorbent with Other Sorbents (All samples were tested at 60,000 h^{-1} in a natural gas mixture containing 12.3 ppmv DMS, 8.9 ppmv TBM and 8.9 ppmv THT at 5 psig)

Table 1. Sulfur Capacities of Sorbents

Sample	Pre-Breakthrough Capacity (% wt.)
TDA's SulfaTrap^{TM}	3.12%
Siemens Sample 5	1.96%
Siemens Sample 4	0.85%
Grace X Zeolite	0.36%
Norit RGM3 Activated Carbon	0.18%

Figure 2 shows the effect of 45 ppmv water vapor on the performance of Norit RGM3 Activated Carbon, unmodified zeolite-X (Grace) and TDA's SulfaTrap^{TM} sorbent. The presence of water reduced the sulfur adsorption capacity of the zeolite-X the most, approximately 83%, showing zeolite-X's high affinity for water vapor. The capacity of the SulfaTrap^{TM} sample remained unaffected from the presence of water vapor in the natural gas feed.

We also measured the sulfur adsorption capacity of the SulfaTrap^{TM} sorbent for 10 consecutive adsorption/regeneration cycles, increasing the bed temperature to 350°C during regeneration. We either

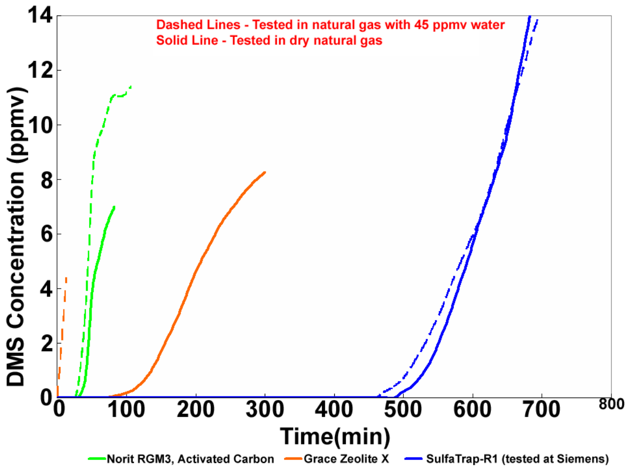

Figure 2. The Effect of Water Vapor on the Performance of TDA's SulfaTrap™ Sorbent and Other Common Sulfur Sorbents (T= 22°C, P= 5 psig, Natural gas with 12.3 ppmv DMS, 8.9 ppmv TBM and 8.9 ppmv THT at 60,000 h^{-1})

used a sulfur-free natural gas or a sulfur-free pre-reformed gas (simulated by hydrogen) to regenerate the sorbent. In both cases, the sorbent maintained a stable total sulfur capacity and DMS capacity through this 10-cycle test [5].

TDA supplied 2.2 L of SulfaTrap^{TM} sorbent to SWPC to support alpha testing of their 5-kW_e SOFC (Figure 3). Test results show that during the 2,700-hr alpha test, TDA's desulfurizer successfully removed all the sulfur from pipeline natural gas (since the sorbent has more capacity, alpha testing of a new SOFC unit will be carried out using the same canister). Based on the successful demonstration results, SWPC requested two more desulfurization units for their 5- and 125-kWe SOFCs.

TDA also modified its sorbent to remove organic sulfur compounds present in the LPG. TDA's sorbent achieves a 2.65% wt. sulfur capacity when used to desulfurize commercial LPG. Less than 20 cc sorbent can desulfurize a 20-lb commercial LPG tank (Figure 4).

Conclusions

A low-cost, high-capacity, regenerable sorbent was developed for removing sulfur-bearing odorants from natural gas at ambient temperature. The sorbent does not interact with hydrocarbons or alter

Figure 3. TDA's Desulfurizer in Combination with SWPC's 5 kWe SOFC during Alpha Testing

Figure 4. TDA's LPG Desulfurization Sorbent

the composition of the natural gas. It does not alter the sulfur compounds that it removes by physical adsorption. It does not contain any toxic ingredients, and it is not pyrophoric. Therefore, it does not require any special handling for disposal if its regenerability is not exploited.

FY 2005 Publications/Presentations

1. "Sorbents for Desulfurization of Natural Gas and LPG," G. Alptekin, Presented at the Annual SECA conference, Pacific Grove, CA, 2005.
2. "Regenerable Sorbents for Desulfurization of Natural Gas and LPG," G. Alptekin, Presented at the Annual American Society of Material Engineers Meeting, Columbus OH, 2004.

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2. A.J. Hernandez-Maldonado and R.T. Yang, "Desulfurization of Diesel Fuels via -Complexation with Nickel (II)-Exchanged X- and Y-Zeolites," Ind. Eng. Chem. Res. 43, 1081-1089, 2004.
3. S. Velu, X. Ma and C. Song, "Selective Adsorption for Removing Sulfur from Jet Fuel over Zeolite-Based Adsorbents," Ind. Eng. Chem. Res. 42, 5293-5304, 2003.
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